

Geochemical Interpretation on Clumped and Position-Specific Isotopes in Natural Gas*

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Abstract

In the past decade some special isotopic compositions of hydrocarbon gas have been measurable and frequently reported, including the clumped isotopic compositions of methane ($\Delta^{13}\text{CH}_3\text{D}$ and $\Delta^{12}\text{CH}_2\text{D}_2$), clumped isotopic composition of ethane ($\Delta^{13}\text{C}_2\text{H}_6$), and position-specific (“intra-molecular”) carbon or hydrogen isotopic compositions in propane or normal butane. As for the interpretation on the data measured from natural gas, most previous works assumed isotopic equilibria, so that these special isotopic compositions can be applied as “geothermometers” of oil and gas accumulations. This assumption contradicts the well-established understanding on petroleum systems, that is, the generation and cracking of hydrocarbons are kinetically controlled (both time and temperature are governing factors), non-equilibrated and continuous processes. There is no single temperature point of hydrocarbon generation, migration, or accumulation. The concepts of “geothermometers” and “equilibrium temperature” are inapplicable to an oil or gas reservoir.

To understand the dependence of clumped and position-specific isotopic compositions on geological and geochemical factors, this work conducts chemical and numerical analyses on isotope distributions during the formation and alteration of oil and gas reservoirs, including biogenic and thermal generation, thermal cracking, and thermochemical sulfate reduction. Because hydrogen atoms in a hydrocarbon molecule come from two precursors during its generation reaction, isotopic compositions involving hydrogen/deuterium (bulk hydrogen isotopic composition δD , clumped isotopic compositions $\Delta^{13}\text{CH}_3\text{D}$ and $\Delta^{12}\text{CH}_2\text{D}_2$, and position specific δD) demand more kinetic analysis on reaction steps and have more complicated fractionation patterns than the carbon isotopic composition $\delta^{13}\text{C}$. Results show that major factors controlling special isotopic compositions are still the same as those controlling conventional ones ($\delta^{13}\text{C}$ and δD) of hydrocarbon gases: precursor, thermal history, and accumulating efficiency (continuous vs. instantaneous accumulation). Temperature is not the only factor determining specific isotopic compositions. Clumped and position-specific isotopic compositions may reverse at high thermal maturity, the same as $\delta^{13}\text{C}$ of ethane and propane, and are even less possible to be applied as “geothermometers”.

Overall, chemical kinetic analyses and numerical simulations are more demanding to interpret clumped or position-specific isotopic compositions than to interpret $\delta^{13}\text{C}$ of natural gas. While these special isotopic compositions may provide more reaction details during hydrocarbon generation, preservation and alteration, oversimplified assumptions and correlations should be avoided during the interpretation.

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Special isotopes and analytical methods

Concepts

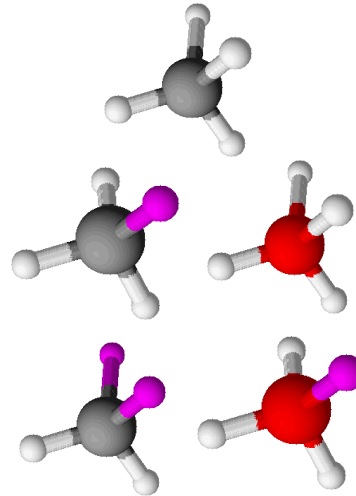
Clumped isotopes

Abundances of methane molecules with two isotopically heavy atoms (double substituted)

Non-substituted: $^{12}\text{CH}_4$

Conventional isotope (bulk isotope):
 Single substitution
 $^{12}\text{CH}_3\text{D}$ and $^{13}\text{CH}_4$

“Clumped isotope”:
 Double substitution
 $^{12}\text{CH}_2\text{D}_2$ and $^{13}\text{CH}_3\text{D}$



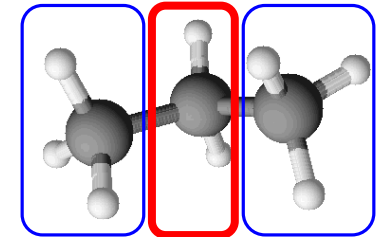
Position-specific isotopes (PSI) of C_3H_8

Difference in $\delta^{13}\text{C}$ between the **middle** and the **end** carbon atoms

$$\delta^{13}\text{C}_{\text{middle}} - \delta^{13}\text{C}_{\text{end}}$$

Difference in δD between the hydrogen atoms connecting to the **middle** and the **end** carbon atoms

$$\delta\text{D}_{\text{middle}} - \delta\text{D}_{\text{end}}$$



Analytical methods

Mass Spectroscopy

$^{13}\text{CH}_3\text{D}$ and $^{12}\text{CH}_2\text{D}_2$: Unresolved (Stolper et al., 2014), Resolved (Young et al., 2017)
 $^{13}\text{C}_2\text{H}_6$ (Clog et al., 2017; for interpretation see Peterson et al., 2018)

PSI $\delta^{13}\text{C}$ after offline enzyme C_3 cleavage (Gao et al., 2016)

PSI $\delta^{13}\text{C}$ after online C_3 pyrolysis (Gilbert et al., 2016)

Laser Spectroscopy

$^{13}\text{CH}_3\text{D}$ (Ono et al., 2014)

Nuclear Magnetic Resonance (NMR)

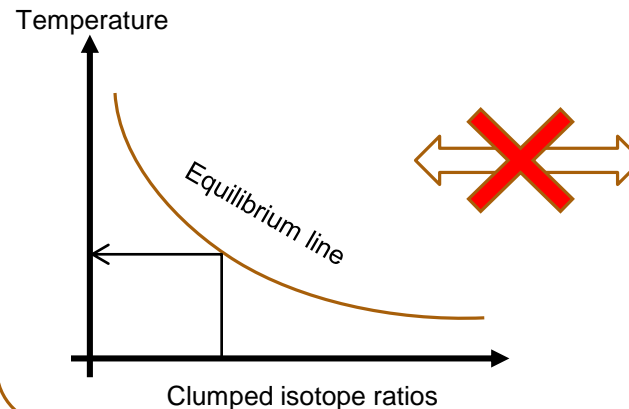
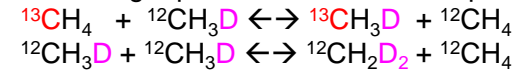
PSI $\delta^{13}\text{C}$ and PSI δD (Liu et al., 2018)

Interpretation towards temperature: contradicts petroleum geology

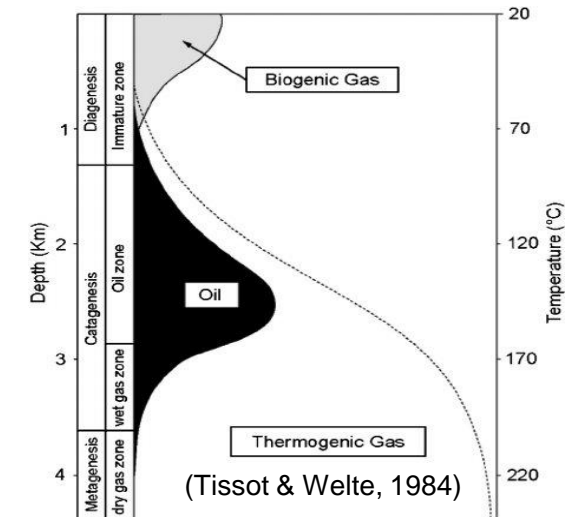
- Most previous interpretations: calculating an “equilibrated temperature” as the generation or charging temperature
- Contradiction to petroleum geological and geochemical observations:
 - Gas generation/expulsion is continuous; no single “generation” or “charging” temperature
 - If it were a temperature equilibrated at some final state in geology, why it’s not the temperature of:
 - Reservoir (especially after cooling due to uplift and erosion)
 - Production
 - Sampling/Storage

Most previous interpretations:

Assuming equilibrium between isotopologues:



Gas generation not at a single temperature!



Isotope distribution during gas generation

- If there is no any interfering factors, clumped isotope distribution is random:

$$\frac{^{13}\text{CH}_3\text{D}}{^{12}\text{CH}_4} = \left(\frac{^{13}\text{CH}_4}{^{12}\text{CH}_4}\right) \left(\frac{^{12}\text{CH}_3\text{D}}{^{12}\text{CH}_4}\right)$$

$$\frac{^{12}\text{CH}_2\text{D}_2}{^{12}\text{CH}_4} = \frac{3}{8} \left(\frac{^{12}\text{CH}_3\text{D}}{^{12}\text{CH}_4}\right)^2$$



Picking up 4 H or D atoms to form a methane molecule

n atoms of H, D/H = x , then xn atoms of D

Ways to form a CH_4 : $\binom{n}{4} = \frac{n!}{4!(n-4)!}$

to form a CH_3D : $\binom{n}{3} \binom{xn}{1} = \frac{n!}{3!(n-3)!} xn$

to form a CH_2D_2 : $\binom{n}{2} \binom{xn}{2} = \frac{n!}{2!(n-2)!} \cdot \frac{(xn)!}{2!(xn-2)!}$

Because n is extremely large,

$$\text{CH}_3\text{D}/\text{CH}_4 = 4x; \text{CH}_2\text{D}_2/\text{CH}_4 = 6x^2$$

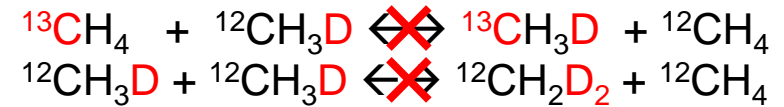
$$\frac{(\text{CH}_2\text{D}_2)(\text{CH}_4)}{(\text{CH}_3\text{D})^2} = \frac{3}{8}$$

Clumped isotopic composition: Definition

- Clumped isotopes defined as deviation from random distribution

$$\Delta^{13}\text{CH}_3\text{D} = \left[\frac{(^{13}\text{CH}_3\text{D})(^{12}\text{CH}_4)}{(^{13}\text{CH}_4)(^{12}\text{CH}_3\text{D})} - 1 \right] \times 1000\text{‰}$$

$$\Delta^{12}\text{CH}_2\text{D}_2 = \left[\frac{(^{12}\text{CH}_2\text{D}_2)(^{12}\text{CH}_4)}{(^{12}\text{CH}_3\text{D})^2} / \frac{3}{8} - 1 \right] \times 1000\text{‰}$$



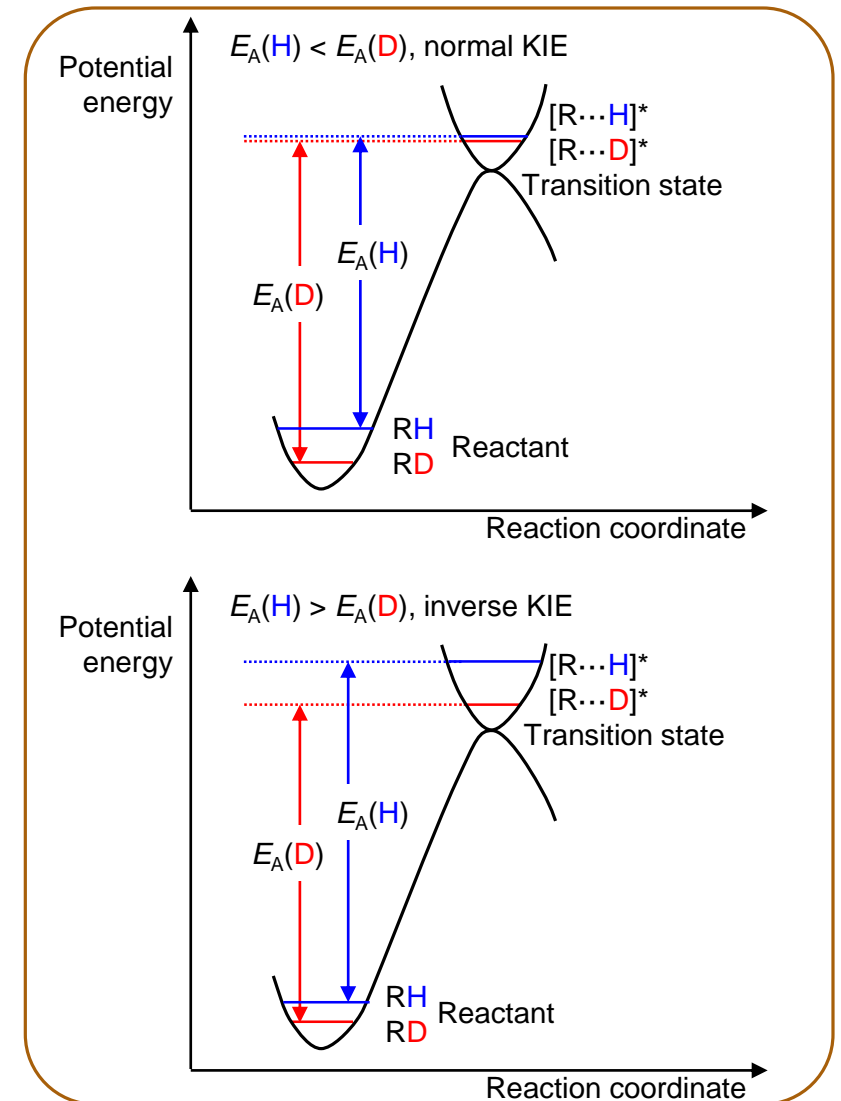
- Not defined as deviation from thermodynamically equilibrated distribution
 - Avoiding presumptions of isotope exchange and equilibrating in many previous papers
 - Deviation from random distribution and deviation from equilibrium are mathematically equivalent
- As the definitions are not relative to a fixed isotope standard (PDB in $\delta^{13}\text{C}$ or SMOW in δD), mixing is not linear

$$\delta_{\text{mix}} = (a \delta_A + b \delta_B) / (a + b) \quad \checkmark \quad \text{..... it works}$$

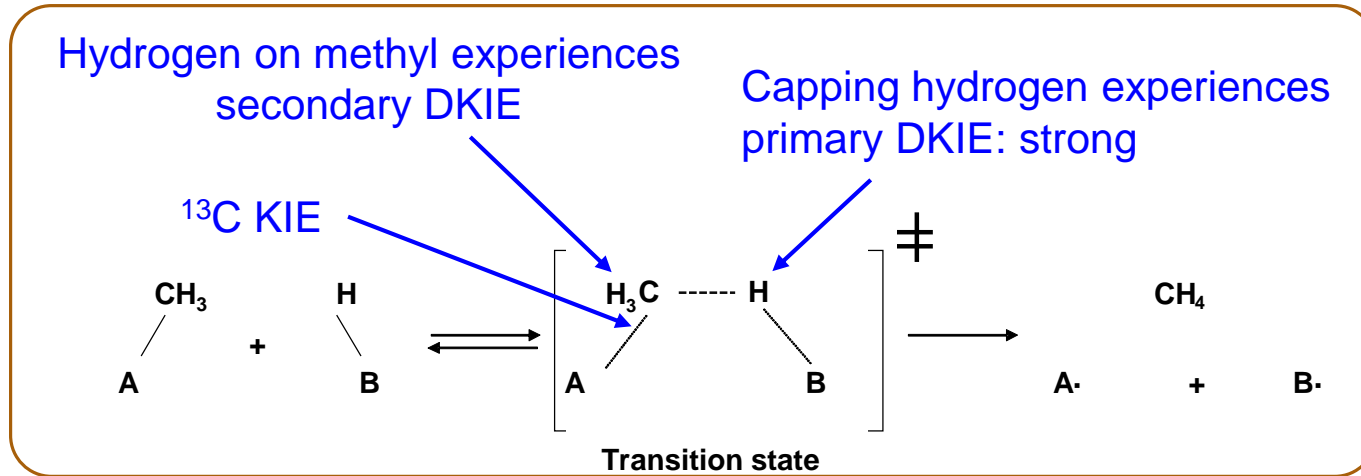
$$\Delta_{\text{mix}} = (a \Delta_A + b \Delta_B) / (a + b) \quad \times \quad \text{..... it doesn't work!}$$

Kinetic isotope effect (KIE): Deviation from random distribution

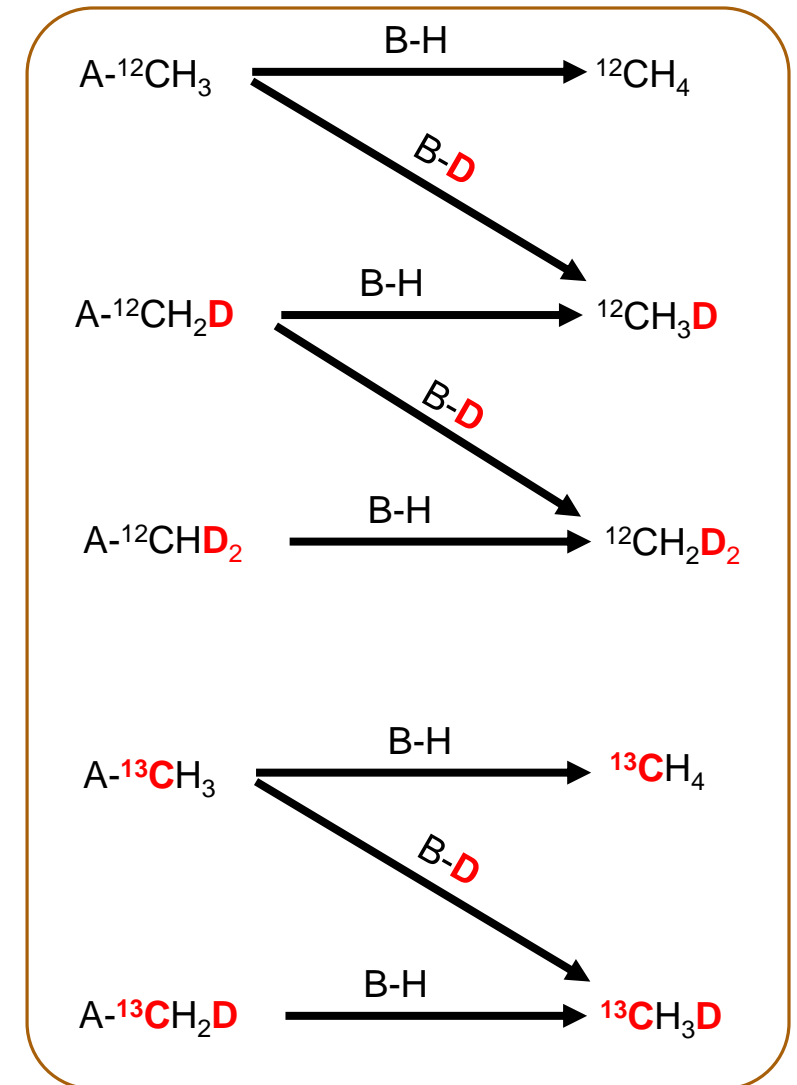
- Normal KIE:
 - ^{13}C - ^{12}C or D - C breaks slower than ^{12}C - ^{12}C or H - C bonds
 - Products more negative in $\delta^{13}\text{C}$ and δD than precursors
- Inverse KIE: Opposite to normal KIE
 - Due to special reaction steps or transition states
 - Not rare in biochemical reactions
 - Possible in thermal cracking, but not well acknowledged in petroleum geochemistry
 - Causing isotope reversal with respect of thermal maturity (“rollover”) or $\delta^{13}\text{C}_{\text{CH}_4} > \delta^{13}\text{C}_{\text{C}_2\text{H}_6} > \delta^{13}\text{C}_{\text{C}_3\text{H}_8} > \delta^{13}\text{C}_{\text{nC}_4\text{H}_{10}}$
 - Not a signature of “abiotic synthesis gas”



KIE during thermal generation of methane



- ^{13}C fractionation: simple; model established (Tang et al., 2000)
- H/D fractionation and clumped isotope distribution
 - Hydrogen has two sources (methyl and capping hydrogen atom)
 - Two kinds of deuterium KIE: primary and secondary DKIE
 - Dramatically more entangled than ^{13}C



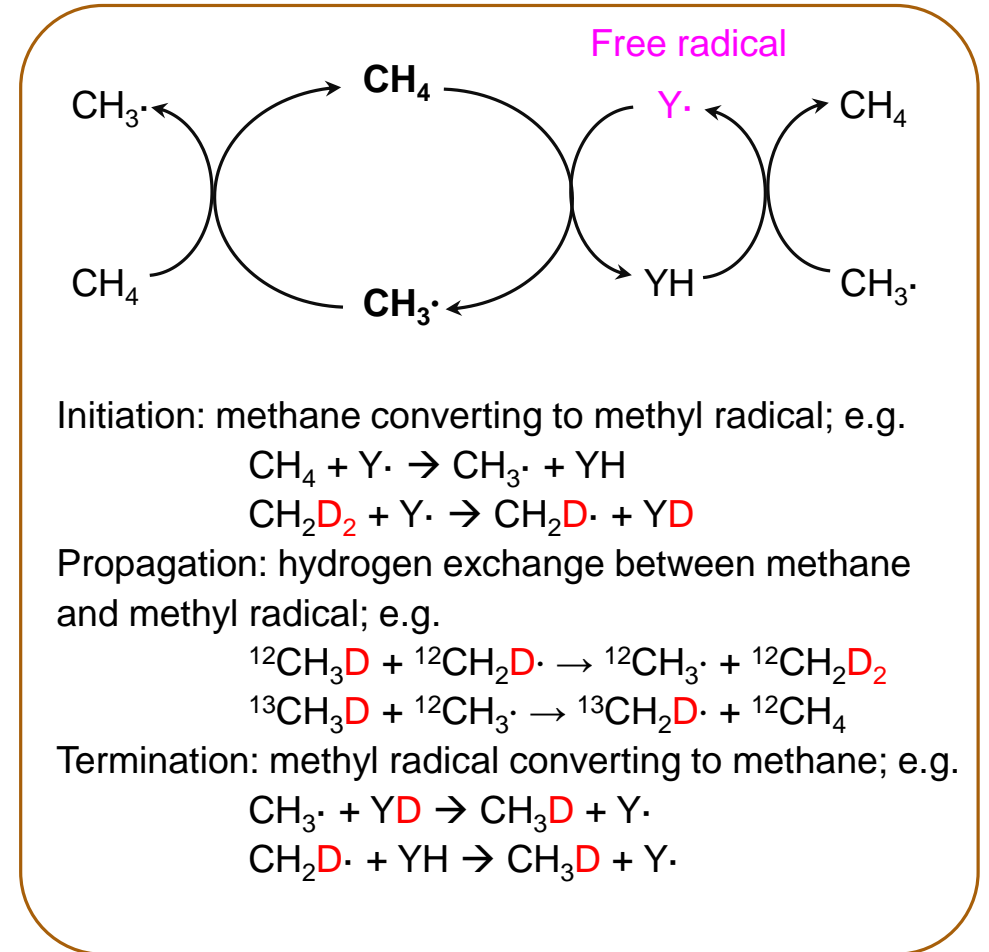
Hydrogen isotope exchange

- Influences δD , $\Delta^{13}CH_3D$ and $\Delta^{12}CH_2D_2$ of methane
- Often oversimplified and inappropriately assumed to be equilibrated, for example:



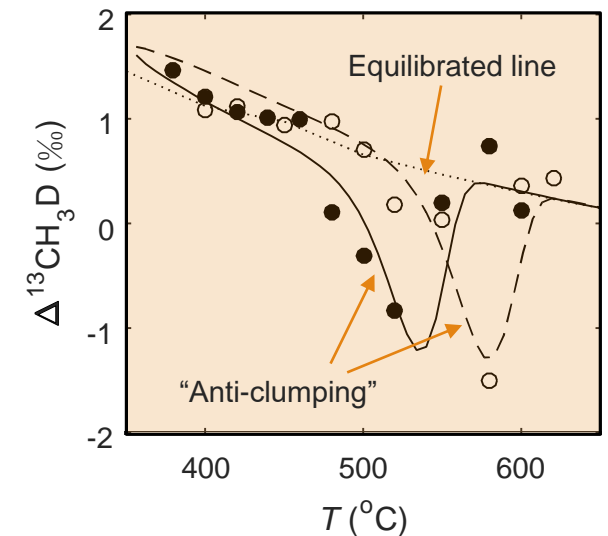
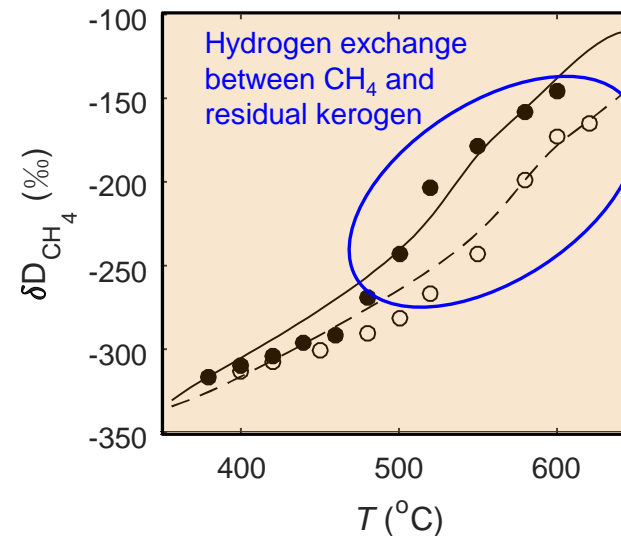
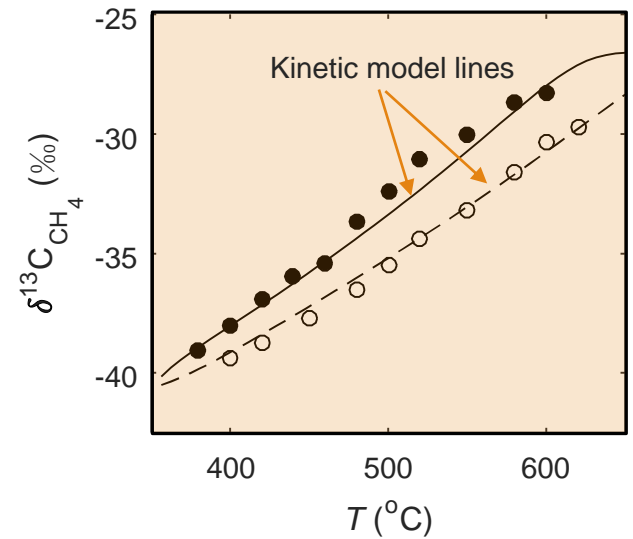
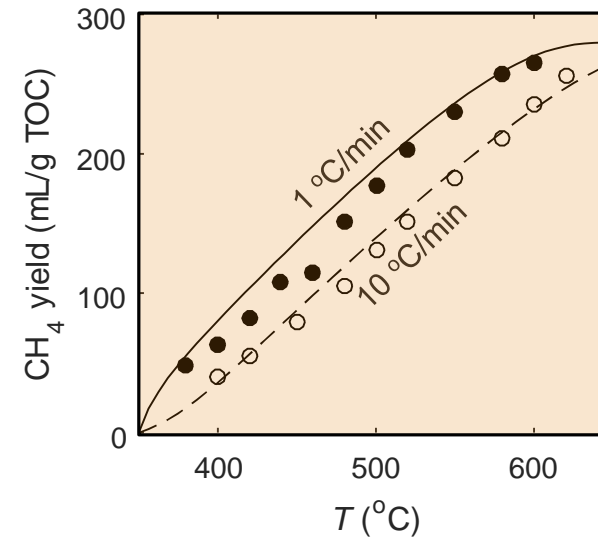
Should be evaluated by investigating detailed reaction steps

- Free radicals on kerogen or pyrobitumen catalyze hydrogen exchange reactions
 - Possible at high thermal maturity or high temperature
 - Accelerate the cracking of ethane and propane in dry gas window (Xia & Gao 2018)



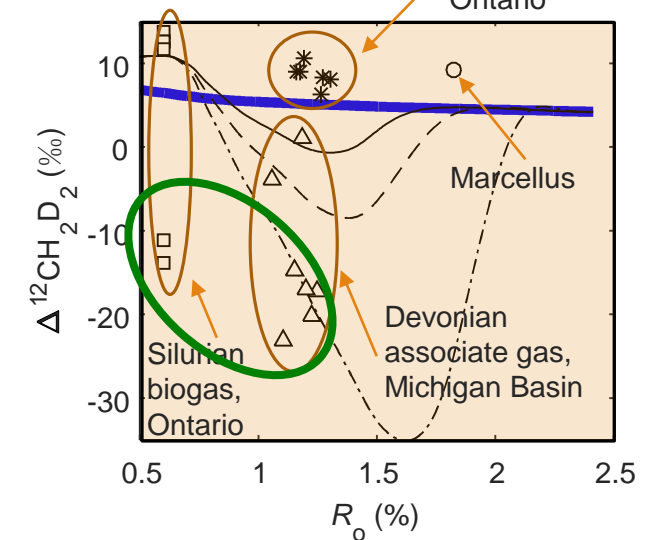
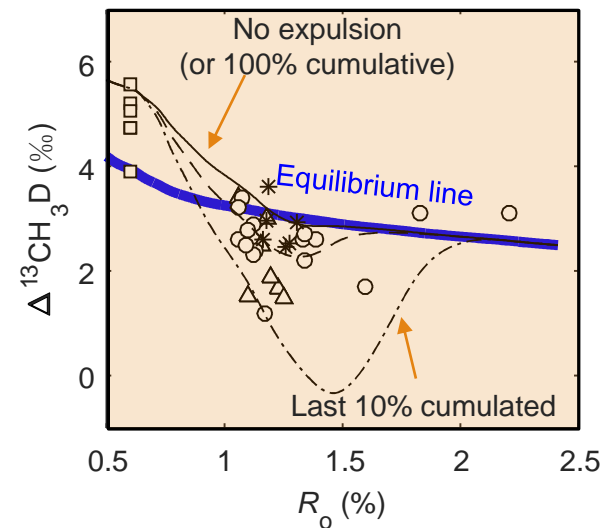
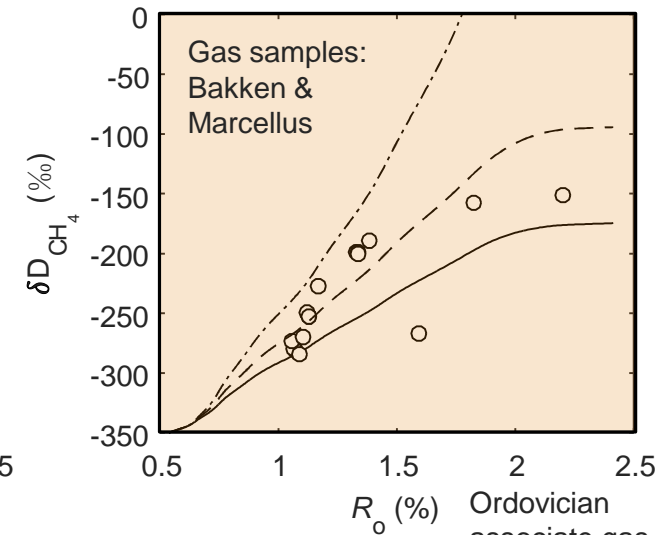
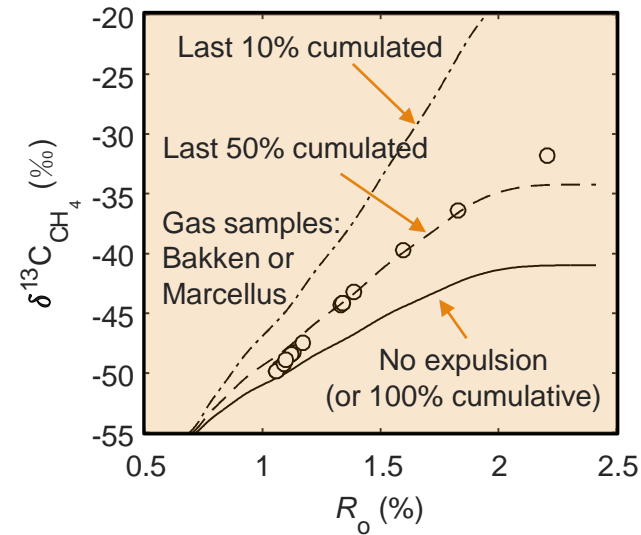
Clumped isotopes of methane from lab pyrolysis

- Methane from coal pyrolysis: clumped isotope disequilibrium revealed (Shuai et al., 2018)
- Kinetic model (parameters well constrained) can explain all the observed phenomena (Xia & Gao, 2019)
 - Jump of δD at high temperature: hydrogen exchange (kerogen as catalyst)
 - Clumped isotopes:
 - Kinetically governed
 - Depletion (anticlumping): because methyl and capping H from two sources
 - Equilibrating due to hydrogen exchange
 - Clumped isotope not a geothermometer



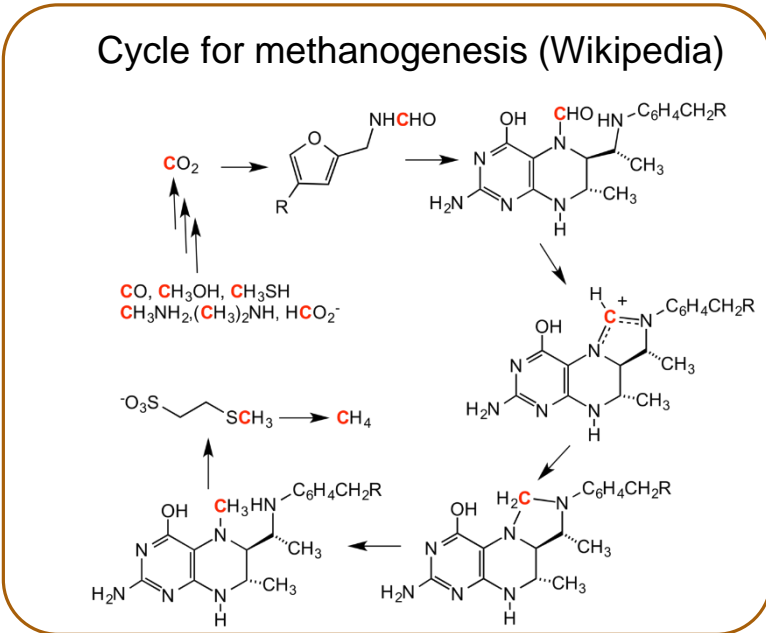
Clumped isotopes of methane in thermogenic gas

- Like other ratios in petroleum geochemistry (e.g. GOR, $C_{7+}\%$, wetness, iC_4/nC_4), isotope ratios are governed by:
 - What chemical reactions occurred: Cracking? Biodegradation? Sulfate reduction?
 - Reaction extent: Transformation ratio (TR) or thermal maturity (R_o)
 - Precursor compositions
 - Extent of accumulation (instantaneous or cumulative?)
- Data can be explained in kinetic isotopic fractionation; not necessarily equilibrated
- Specialty of clumped isotopes: not simply increase or decrease with thermal maturity (nonmonotonic)
 - Reason: anticlumping; hydrogen exchange; non-linear mixing

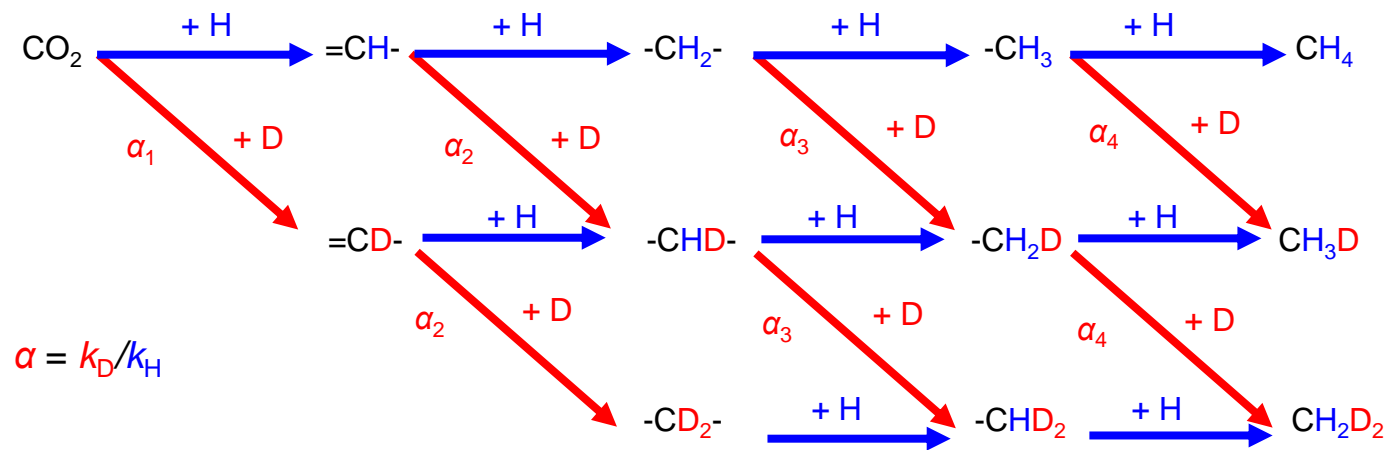


CH₂D₂ depletion in microbial methane

- Four hydrogenation steps from CO₂ to CH₄ (methanogenesis)
- If some steps have stronger or weaker DKIEs than the others, then CH₂D₂ depletion occurs
 - Suppose $\alpha_1 = 0.6$, $\alpha_2 = \alpha_3 = \alpha_4 = 1$, then $\Delta^{12}\text{CH}_2\text{D}_2 = -\left(\frac{1-\alpha}{3+\alpha}\right)^2 = -12\text{‰}$ (same if $\alpha_1 = \alpha_2 = \alpha_3 = 0.6$, $\alpha_4 = 1$)
 - Suppose $\alpha_1 = \alpha_2 = 0.6$, $\alpha_3 = \alpha_4 = 1$, then $\Delta^{12}\text{CH}_2\text{D}_2 = -\frac{1}{3}\left(\frac{1-\alpha}{1+\alpha}\right)^2 = -21\text{‰}$
 - Explanation with a strong DKIE ($\alpha < 0.1$) from “Quantum Tunneling Effect” is unnecessary!



$$\Delta^{12}\text{CH}_2\text{D}_2 = -\frac{(\alpha_1 - \alpha_2)^2 + (\alpha_1 - \alpha_3)^2 + (\alpha_1 - \alpha_4)^2 + (\alpha_2 - \alpha_3)^2 + (\alpha_2 - \alpha_4)^2 + (\alpha_3 - \alpha_4)^2}{3(\alpha_1 + \alpha_2 + \alpha_3 + \alpha_4)^2} \times 1000\text{‰}$$

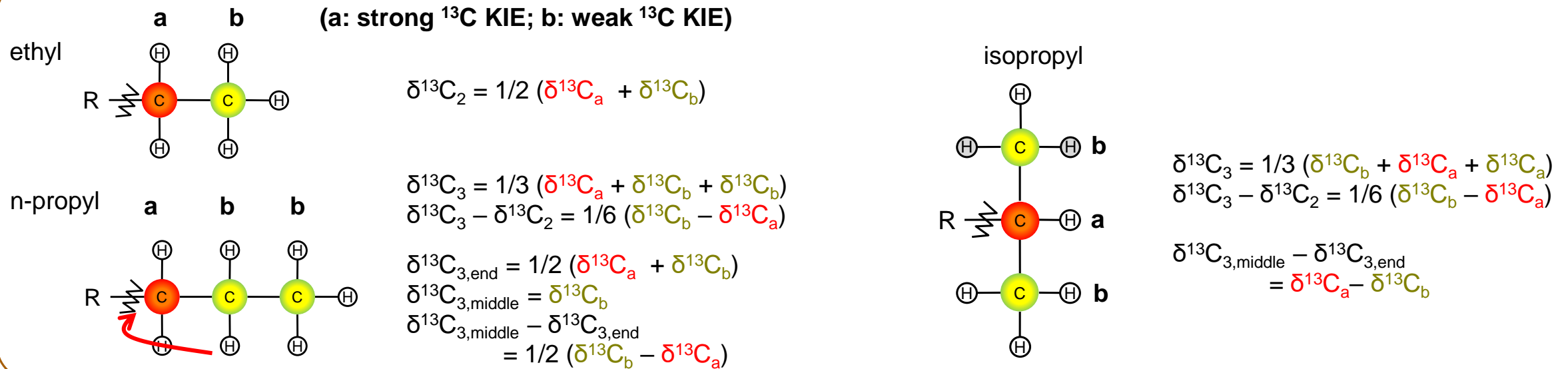


Position-specific isotope (PSI) fractionation: depending on reaction steps of C₃H₈ generation

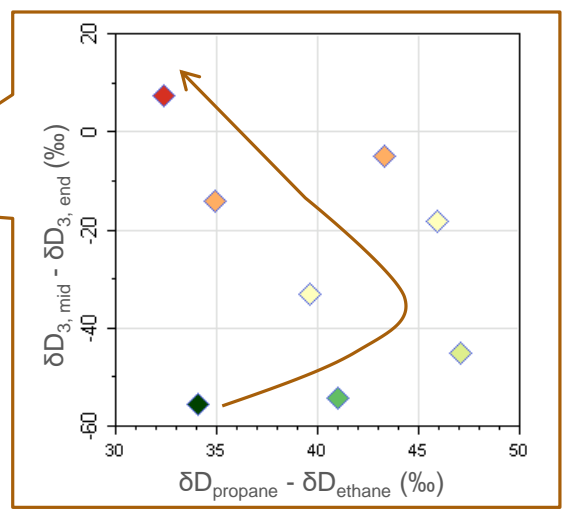
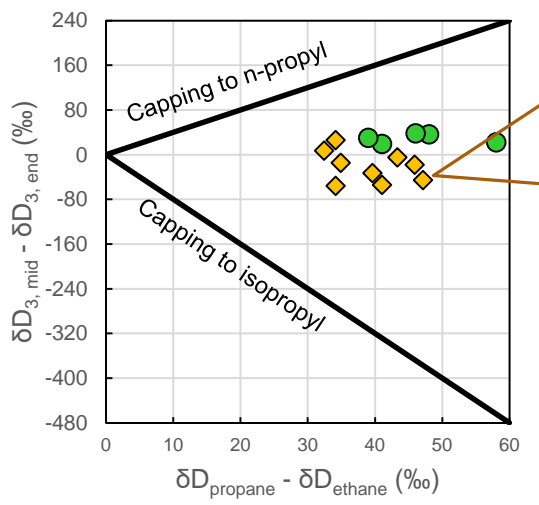
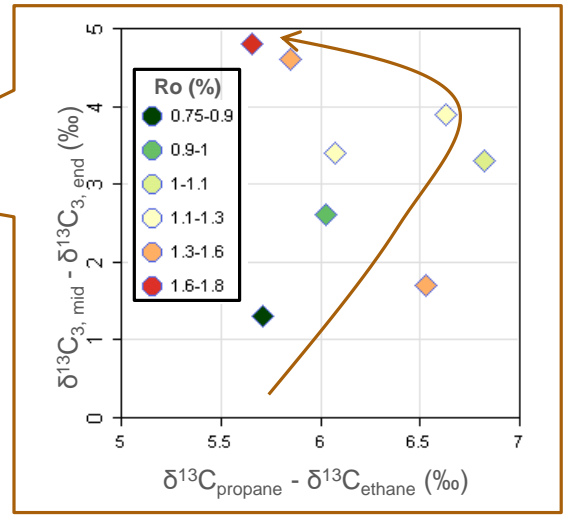
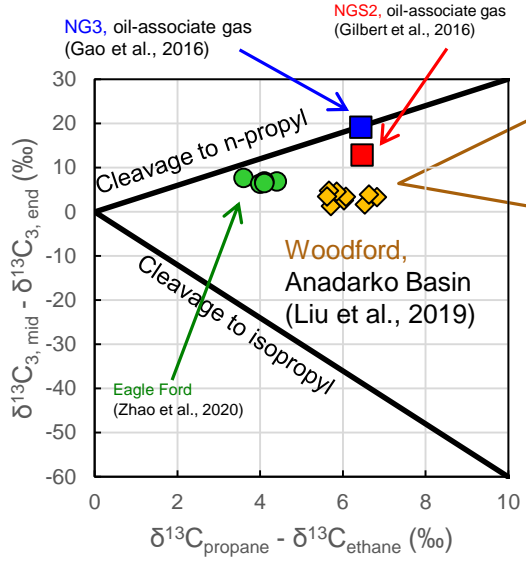
Correlating the position-specific isotope to conventional isotopes

(This analysis follows Chung et al. 1988)

Reaction mechanism	$\delta^{13}\text{C}_{3, \text{middle}} - \delta^{13}\text{C}_{3, \text{end}}$	$\delta\text{D}_{3, \text{middle}} - \delta\text{D}_{3, \text{end}}$
Kerogen → n-propyl → propane (cracking) (hydrogen shift) (hydrogen capping)	$3(\delta^{13}\text{C}_{\text{propane}} - \delta^{13}\text{C}_{\text{ethane}})$ (Xia & Gao, 2017)	$4(\delta\text{D}_{\text{propane}} - \delta\text{D}_{\text{ethane}})$
Kerogen → n-propyl → isopropyl → propane		$-8(\delta\text{D}_{\text{propane}} - \delta\text{D}_{\text{ethane}})$
Kerogen → isopropyl → propane	$-6(\delta^{13}\text{C}_{\text{propane}} - \delta^{13}\text{C}_{\text{ethane}})$	



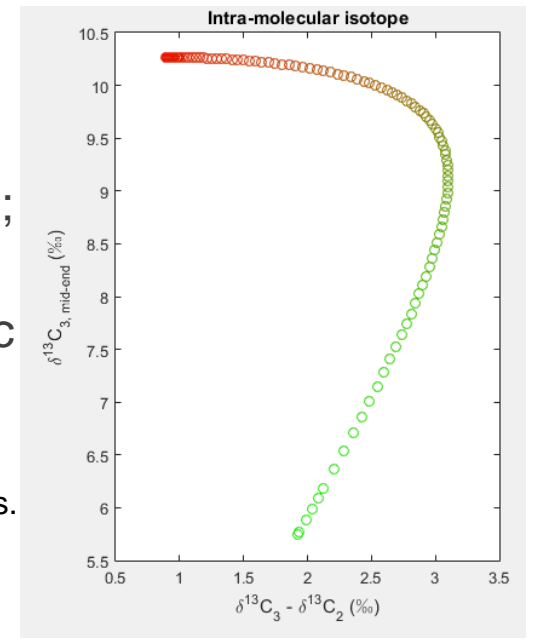
Interpreting position-specific isotope (PSI) during propane generation



- PSI $\delta^{13}\text{C}$: majority of propane is from n-propyl
- PSI δD : n-propyl \rightarrow isopropyl (hydrogen shift) is common
- Inverse trends explainable with a random distribution of cracking position on kerogen side chains
- Don't overinterpret (esp. with a mixing model) any isotope reversal trends; they may just from intrinsic behaviors of a single kinetic process!

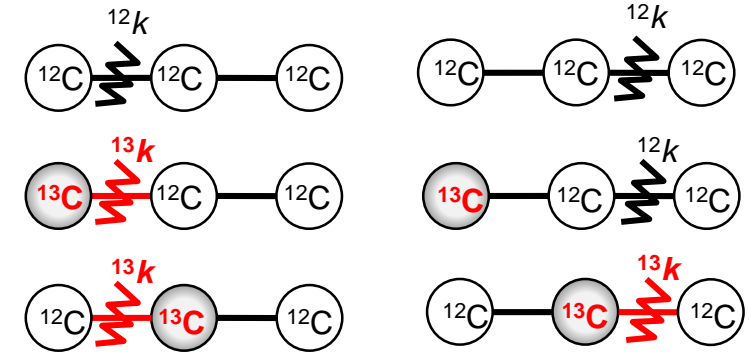
Modeling results of random cutting on kerogen side chains.

For a random cutting model see Peterson et al. (2018).

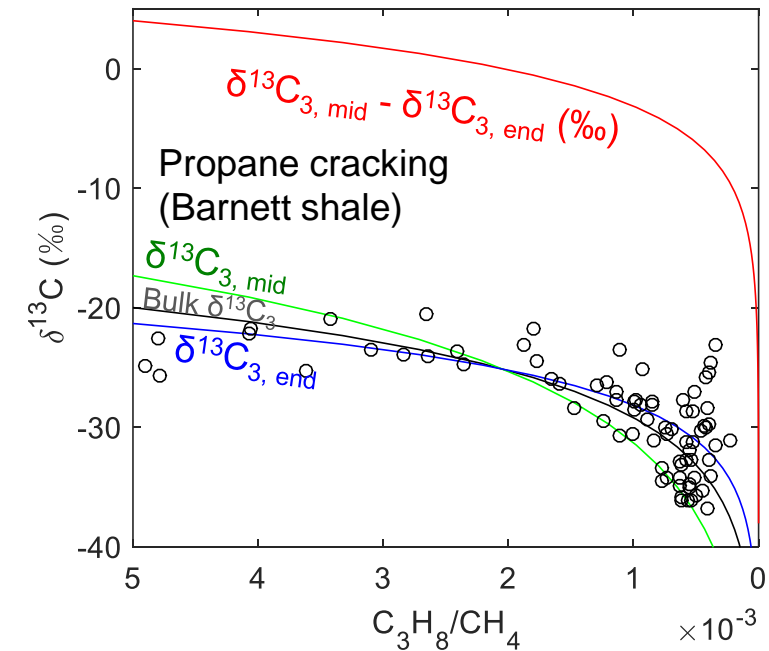
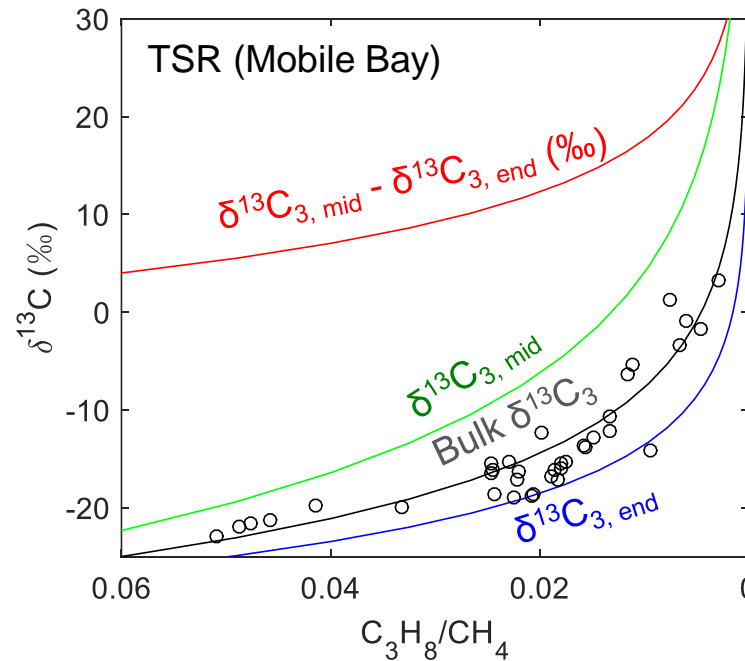


PSI $\delta^{13}\text{C}$ of residual propane during thermal cracking and during thermochemical sulfate reduction (TSR)

- Scheme of isotope fractionation: ^{13}C substitution has KIE on the activation of adjacent C-C bond(s)
- Expected results: PSI $\delta^{13}\text{C}$ trends resemble bulk $\delta^{13}\text{C}$
 - Enrichment of ^{13}C in the middle carbon due to normal ^{13}C KIE during TSR
 - Depletion (or “rollover”) of the middle carbon due to inverse ^{13}C KIE during propane cracking in dry gas window



Bulk $\delta^{13}\text{C}_{\text{propane}}$ data from Mankiewicz et al. (2009) and Zumberge et al. (2012); for reaction mechanisms see Xia et al. (2014); Xia and Gao (2018).



Summary: role of special isotopes in petroleum geochemistry

- Clumped isotope answers:
“Have atoms in each molecule experienced an identical chemical process?” If depletion: No
- Position-specific isotope answers:
“Do atoms in each molecule have an identical KIE?” If intra-molecular fractionation: No
- May improve understanding geochemical signatures during hydrocarbon generation/alteration (reaction steps; hydrogen exchange; isotope fractionation), rather than provide direct additional information for routine petroleum systems analysis (kerogen type, thermal maturity, generating/charging time, accumulation efficiency)
- Data interpretation requires chemical kinetic analysis and numerical simulations
- Empirical correlations, oversimplifications and unrealistic assumptions (esp. equilibrium) result in misinterpretations
 - Not as a “geothermometer” for hydrocarbon generation or charging

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